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THE CONFIGURATIONAL INVERSION OF METHYL-SUBSTITUTED 1,1'-BINAPHTHYLS AS STUDIED BY MOLECULAR MECHANICS

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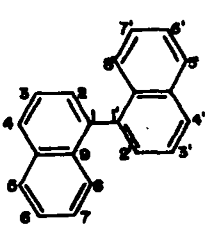
Abstract—The striking difference in optical stability between 2- and 2,2'-substituted 1,1'-binaphthyls on the one hand, and the corresponding 8- and 8,8'-substituted compounds on the other, has been investigated with the aid of the molecular mechanics method. The calculations suggest reasonable sources of energy differences in both initial and transition states for the pairs of molecules studied, and clearly implicate the *peri* effect as an important contributor to the increased optical lability of the 8- and 8,8'-substituted compounds.

The application of the molecular mechanics method[1] to calculations of the energies and probable conformations involved in the configurational inversion of 1,1'-binaphthyl[2] gave quantitative results entirely compatible with the available experimental data, and provided insight into the details of the inversion process (in particular in the transition state region). In view of these encouraging results on 1,1'-binaphthyl itself, we have now extended our calculations to the 2-, 2,2'-, 8- and 8,8'-Me substituted derivatives in an attempt to gain detailed information on the reason(s) for the much greater optical stability in the 2,(2')- than in the 8,(8')-compounds. For example, 2-hydroxy-1,1'-binaphthyl and the corresponding acid succinate derivative were found by Berson and Greenbaum[3] to have approximate half lives of two days and two weeks, respectively, in boiling benzene. Hall and Turner[4] reported that the 2,2'-dicarboxylic acid, as well as the 2,2'-hydroxymethyl and 2,2'-bromomethyl compounds, failed to racemize after 8 hr at 175° (no observable change in optical activity: cf. also work by Kuhn and Albrecht[5] on the dicarboxylic acid). More recent work by Dixon *et al.*[6f] includes the observation that the specific rotation of 2,2'-dimethyl-1,1'-binaphthyl remained unchanged after 40 hr in 1-methylnaphthalene solution at 240°. The striking optical lability of compounds in the 8- and 8,8'-series has been discussed and studied in great detail by Harris *et al.*[6] "Classical" models (i.e. planar and rigid aromatic rings) are utterly incapable of providing a rationalization for these observations. Harris *et al.*[6] originally suggested the difference in optical stability to be primarily due to initial-state *peri* interactions in the 8,(8')-series, with concomitant increase of the initial-state energy and lowering of the barrier to configurational inversion. As will be described below, the calculations partly confirm this suggestion, but—with judicious interpretation—are found capable of providing a more nuanced picture of the inversion process than previously possible, including both initial- and transition-state effects.

The method of calculation, using the molecular mechanics program developed by Allinger *et al.*,[1d] was described in the previous paper,[2] to which the reader is referred for details. In the present work, the dihedral angle as a function of which the conformational energies were calculated (the "driving angle")[2,7] was the same in all cases, viz the C_9–C_1–$C_{1'}$–$C_{2'}$ angle. (In the numbering system shown below, the Me groups in the two mono Me compounds are thus placed in the 8- and 2'-positions, respectively.)



Furthermore, only inversion pathways involving rotation toward the *anti* ("*trans*") configuration were taken into consideration, since *syn* inversion paths were previously found,[2] as expected, to be of much higher energy and thus incompatible with the experimentally observed enthalpy of racemization in the case of 1,1'-binaphthyl.[6b,8]

In analogy with our previous work,[2] all of the transition-state model calculations were initiated at a dihedral angle corresponding to a local potential energy minimum (Fig. 1). The conformation in this local minimum is essentially equivalent to the "mesoid" intermediate structure suggested by Harris *et al.*[6] to lie along the lowest energy pathway for configurational inversion in the 8,8'-disubstituted compounds. (In the monosubstituted compounds, the term "mesoid" is of course a misnomer due to the lack of symmetry, but according to our calculations there nonetheless exists a local minimum between two (different) transition states even in these cases.)

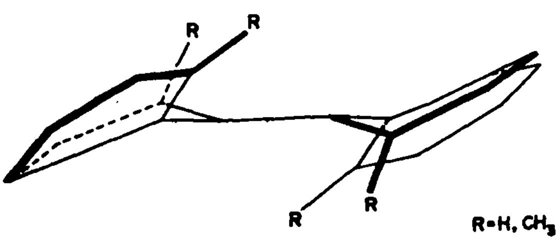


Fig. 1. Local minimum conformation of 8,(8')- and 2,(2')-substituted 1,1'-binaphthyls (see also Fig. 3, IV in Ref. 2).

RESULTS AND DISCUSSION

2- and 8-Methyl-1,1'-binaphthyl.† The initial-state potential minimum for these molecules is calculated to be rather broad and shallow (as in the case of binaphthyl itself[2]) with energy minima at dihedral angles of 110° and 114.7° for the 2- and 8-substituted compounds, respectively. The minimum for 8-Me–BN is found to lie 3.1 kcal/mol above that for the 2-Me analog, primarily as the result of molecular deformations arising in connection with the *peri* effect[9] between the 8-Me group and the 1'-C atom (Figs. 2 and 3).

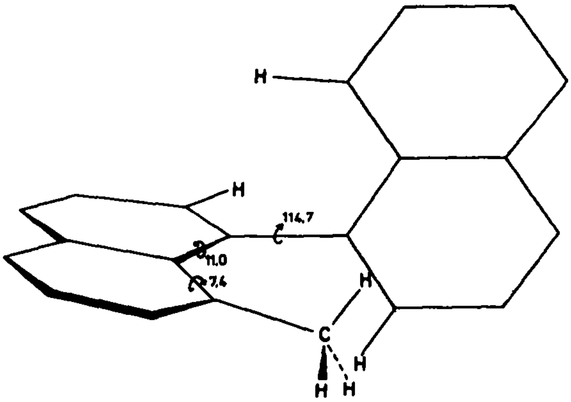


Fig. 2. Calculated initial-state geometry of 8-methyl-1,1'-binaphthyl.

In our calculations, distortion attributable to the *peri* effect has been generally found to be of considerable importance in the determination of relative conformational energies. Experimental estimates of this effect have apparently not been made for molecules in the 1,1'-binaphthyl series, but *peri* strain in Me-substituted naphthalenes has been studied by Packer *et al.*[10] using a kinetic method based on the Menschutkin reaction of analogous quinoline compounds, and by Månsson,[11] who employed the more straightforward (but experimentally more demanding) method of direct calorimetric measurement. Packer *et al.*[10] estimated the strains present in 1-methyl-, 1,2-dimethyl- and 1,8-dimethylnaphthalene to be 1.6, 3.4 and 7.6 kcal/mol, respectively. The relevant comparison for our purposes is between the 1,2-dimethyl- and 1,8-dimethyl compounds, the first of which may be considered to establish the zero of the energy scale. In this way, the *peri* strain in 1,8-dimethylnaphthalene is found to be approximately 4.2 kcal/mol, which is in reasonably good agreement with Månsson's thermodynamically estimated values[11] of 5.7 and (6.2 ± 1.4) kcal/mol. In the 8-Me–BN system, the *peri* strain is expected to be somewhat less, since the interaction is between a methyl group and an effectively smaller sp^2-hybridized aromatic carbon. Our calculated figure of 3.1 kcal/mol thus appears quite plausible in this context.

The passage through the transition state (Me···H nonbonded contact) occurs at a dihedral angle of about 48° in both the 2- and 8-substituted molecules, but the 2-Me–BN transition state is calculated to be 7.1 kcal/mol higher in energy than that for the 8-Me compound. The total energy barrier difference in this case is thus 10.2 kcal/mol. No experimental value for this difference is apparently available for comparison, but the calculated figure is certainly in accord with the well-documented[3-6] large difference in optical lability between 2- and 8-substituted 1,1'-binaphthyls. The energy difference between the initial and transition states is calculated to be 22.5 kcal/mol for the 8-Me compound, and 32.7 kcal/mol for the 2-Me isomer. (The calculated energies and available experimental data are summarized in Table 1.) 8-Methyl-1,1'-binaphthyl was prepared in optically active form by Cooke and Harris,[6d] who report a value of 24.6 kcal/mol for the enthalpy of racemization ($\Delta H^{\neq}$) in N,N-dimethylformamide solution. The satisfactory agreement between the experimental and theoretical energy barrier values for 8-Me–BN lends some confidence to the value obtained for the 2-Me compound.

We further note by way of comparison that the

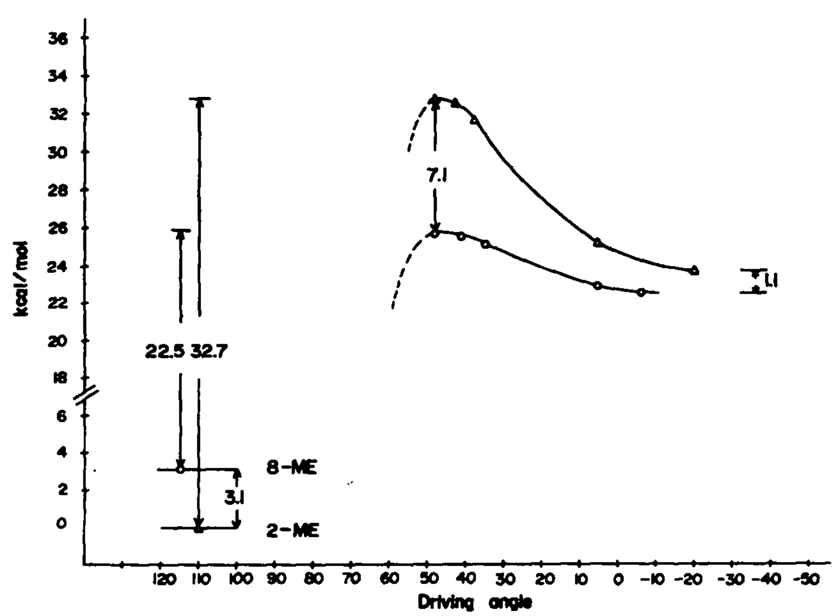


Fig. 3. Calculated energies vs driving angle (C_9–C_1–$C_{1'}$–$C_{2'}$) for 2- and 8-methyl-1,1'-binaphthyl.

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†Abbreviation: 1,1'binaphthyl = BN.

Table 1. Calculated and experimental barriers to configurational inversion and barrier increments based on 1,1'-binaphthyl

Compound	Barrier, kcal/mol Calc'd	Barrier, kcal/mol Expt'l ($\Delta H^{\neq}$)	Barrier Increments, kcal/mol Calc'd	Barrier Increments, kcal/mol Expt'l ($\Delta\Delta H^{\neq}$)
1,1'-Binaphthyl	20.4^2	21.9^{6b} $(21.5\pm0.2)^8$	0.0	0.0
2-Methyl-BN	32.7	-	+12.3	-
2,2'-Dimethyl-BN	34.9	-	+14.5	-
8-Methyl-BN	22.5	24.6^{6d}	+ 2.1	+2.7
8,8'-Dimethyl-BN	23.0	26.8^{6c}	+ 2.6	+4.9

experimental increment in $\Delta H^{\neq}$ between 1,1'-binaphthyl itself and the 8-Me compound is +2.7 kcal/mol,[6b,d] while the corresponding calculated increment is 22.5–20.4,[2] or 2.1 kcal/mol (Table 1).

A point of interest in the present context is that the transition-state energy difference is calculated to be more than twice as large as the initial-state difference and in the opposite direction, and thus (at least in this case) *initial-state* strain is not the only important factor behind the optical lability of the 8-methyl compound. Of even more importance, according to the picture resulting from our calculations, is the greater ease with which the effects of steric crowding may be alleviated in the transition state for 8-Me–BN than in that of 2-Me–BN (Figs. 4 and 5 for details). In the 2-Me compound, twisting about the C_2–C_1, C_1–C_9, $C_{2'}$–$C_{1'}$, $C_{1'}$–$C_{9'}$ and $C_{9'}$–$C_{8'}$ bonds is appreciable, and all four of the angles which include the 1,1'-bond deviate considerably from their initial state values, as the naphthyl residues bend away from each other to minimize steric compression in the transition state. In contrast, in the 8-Me case, twisting is confined primarily to four C–C bonds (instead of five), and only two of the angles which include the 1,1'-bond (C_9–C_1–$C_{1'}$ and $C_{2'}$–$C_{1'}$–C_{1}) deviate markedly from the ideal value of 120°. In both transition-state models, the torsional contribution to the steric energy predominates, but this contribution is greater by 3.3 kcal/mol in the 2-Me than in the 8-Me compound. In addition, the contribution of bending distortions to the steric energy is 3.5 kcal/mol greater in the former than in the latter.

Part of the transition-state energy difference of 7.1 kcal/mol is a direct consequence of the initial-state *peri* effect in the 8-Me compound. Since the molecule is already distorted in the initial state, the additional dis-

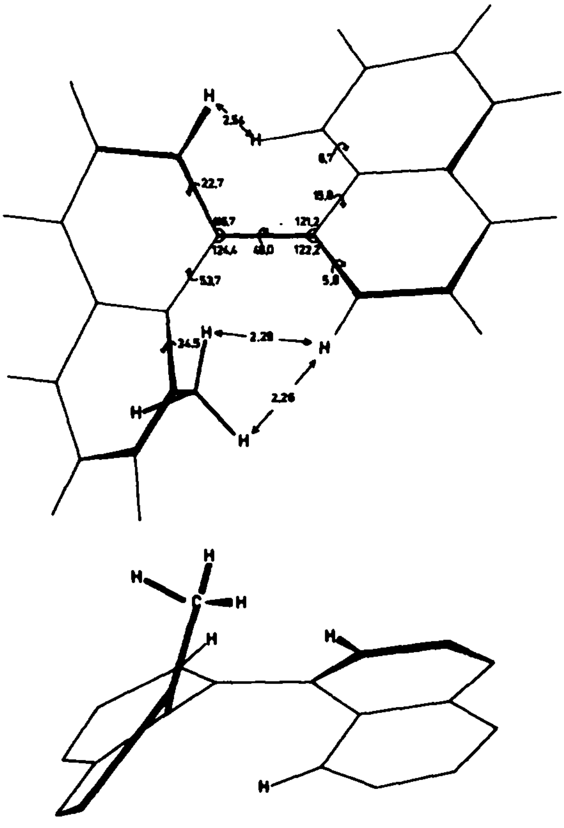

Fig. 4. Calculated transition-state geometry of 8-methyl-1,1'-binaphthyl.

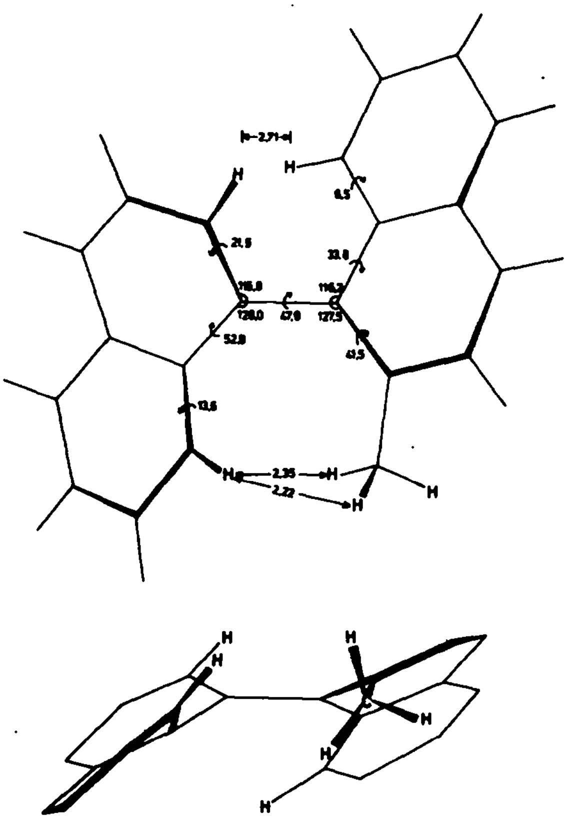

Fig. 5. Calculated transition-state geometry of 2-methyl-1,1'-binaphthyl.

tortion required to reach the transition state is less than in the 2-Me case.[12] The deformations in the 8-Me transition state tend to diminish the repulsive nonbonded interactions due to the *peri* effect and thus lower the energy relative to that in the 2-Me compound, where almost all of the requisite deformations for the inversion process are relegated to the transition state. In this case, there is no *peri* effect to facilitate transition-state deformation.

2,2'- and 8,8'-Dimethyl-1,1'-binaphthyl. Due to the predominance of the *peri* effect in the determination of the relative positions of the initial-state energy levels, the initial-state difference between the 2,2'- and 8,8'-dimethyl compounds (6.7 kcal/mol) is about twice that between the mono Me analogs. This additivity does not however carry over to the transition state; indeed, the transition-state difference is somewhat *less* in the dimethyl case than in the mono Me (Fig. 6). The transition-state energy difference decreases from 7.1 kcal/mol (2- vs 8-Me) to 5.2 kcal/mol (2,2'- vs 8,8'-dimethyl). In the 8,8'-dimethyl case, the increased van der Waals repulsion on the "passing side" of the molecule cannot be compensated by the release of distortions on the opposite side, as this leads to increased *peri* interactions.† In the 2,2'-dimethyl transition state, on the other hand, such an effect does not operate, and we are led to the conclusion that the introduction of an 8'-Me group into the 8-Me–BN system *raises* the transition-state energy by a larger amount than the corresponding change in the 2-Me case. The fact that the 2,2'-transition state nonetheless lies 5.2 kcal/mol above that for the 8,8'-transition state is in the final analysis the consequence of the overall greater ease with which steric crowding on the *passing* side may be diminished in the latter case than in the former. An analogous difference was mentioned above in the presentation of the results for the 2- and 8-Me compounds.

A further point of interest is that the calculated local minimum, which occurs at a dihedral angle (C_9–C_1–C_1–$C_{2'}$) of −15° in 2,2'-dimethyl–BN, lies 4.5 kcal/mol above the corresponding point for 8,8'-dimethyl–BN (at a dihedral angle of −6°; see Fig. 6). Due to symmetry, the dihedral angle on the opposite side of the molecule ($C_{2'}$–C_1–C_1–C_9) is identical with the C_9–C_1–C_1–$C_{2'}$ angle in the disubstituted molecules. In the 2- and 8-Me compounds, where the local minima are separated by only 1.1 kcal/mol, the difference in the dihedral angles C_9–C_1–C_1–$C_{2'}$ and $C_{2'}$–C_1–C_1–C_9 is only 2° in the 8-Me case (−7° and −9°, respectively), whereas it is as large as 19° in 2-Me–BN (−20° and −1°, respectively). This clearly indicates that the alleviation of steric repulsions in the 2-Me–BN local minimum requires not only skeletal distortions, as in the 8-Me case, but also rotation about the 1,1'-bond. The latter mode of relaxation is not available to the 2,2'-dimethyl compound because of symmetry. In these terms, the larger difference in energy between the local minima in the disubstituted molecules than in the monosubstituted ones (4.5 vs 1.1 kcal/mol) receives an adequate rationalization.

In all of the models for the local minima, there is calculated to be appreciable bending of the naphthyl residues away from each other at the 1,1'-bond (Fig. 1).

The height of the barrier to configurational inversion is calculated to be 23.0 kcal/mol in the 8,8'-dimethyl compound, only 0.5 kcal/mol above that for 8-Me–BN, and is to be compared with a value of 26.8 kcal/mol ($\Delta H^{\neq}$), determined by Badar *et al.*,[6c] which is 2.2 kcal/mol above the corresponding value of 8-dimethyl–BN. The additivity of the experimental energy barrier increments as 8- and 8'-Me groups are introduced into the 1,1'-binaphthyl skeleton (+2.7 kcal/mol for the first and an additional +2.2 kcal/mol for the second) was attributed by Cooke and Harris[6d] to an assumed additivity of the initial-state *peri* effect. The experimentally observed additivity in the energy barrier does not emerge from the calculations; we find +2.1 kcal/mol for the first Me group and an additional +0.5 kcal/mol for the second (Table 1). In view of the previously demonstrated ability of the calculational method to quantitatively reflect the experimental observations,[2] this discrepancy deserves

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†It should be borne in mind that in making the transition-state calculations, the driving angle begins at the value corresponding to the local minimum.

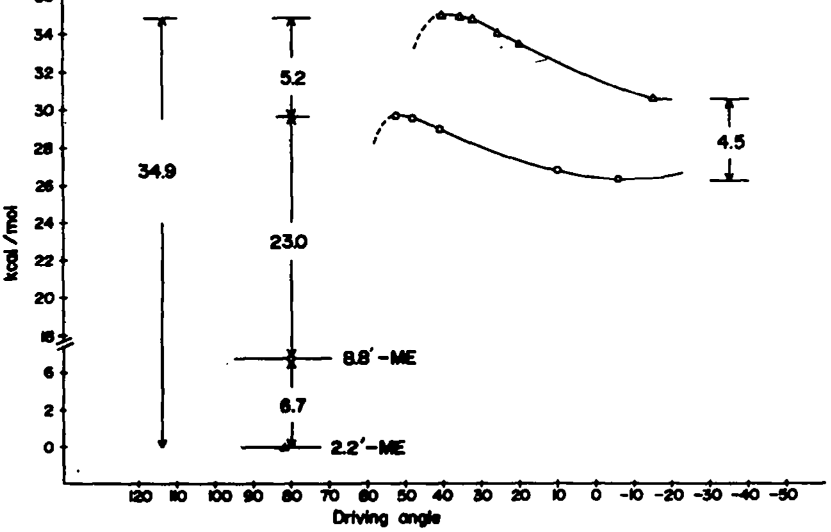

Fig. 6. Calculated energies vs driving angle (C_9–C_1–C_1–$C_{2'}$) for 2,2'- and 8,8'-dimethyl-1,1'-binaphthyl.

some comment. The insertion of a Me group in the 8'-position of the calculated transition-state structure for 8-Me–BN (Fig. 4) would *a priori* be expected to have a minimal effect on the steric energy of the transition state (*one point* of nonbonded contact; see Fig. 7), and not an effect on the order of 4 kcal/mol, which is the experimental result if the observed increments in $\Delta H^{\neq}$ are attributed solely to *initial-state* strain. (Note that the model predicts essentially the same dihedral angle for the 8-Me and 8,8'-dimethyl transition states; see Figs. 3 and 6.) In the 2,(2')-compounds, the lack of additivity according to our calculations is even more striking: compared to 1,1'-binaphthyl itself, the first methyl group in the 2-position leads to an energy barrier increment of 12.3 kcal/mol, while the second Me group is calculated to result in a further increment of only 2.2 kcal/mol. The calculated barrier to configurational inversion in 2,2'-dimethyl–BN is 34.9 kcal/mol, which is comparable to an estimate by Badar *et al.*[6c] of the Arrhenius activation energy for the racemization of this compound (37–40 kcal/mol). The only available experimental data on 2,2'-dimethyl–BN,[6f] referred to above in the introductory section of this paper, are certainly compatible with a barrier as high as 40 kcal/mol, provided a (reasonable) value of $\Delta S^{\neq}$ of the order of -10 to -12 cal/(mol K) is assumed. The calculated transition-state structure for the 2,2'-compound is shown in Fig. 8.

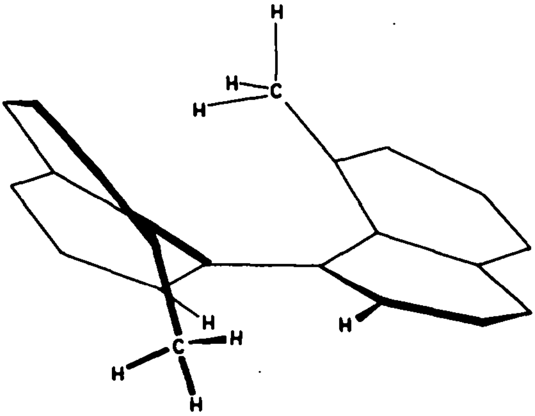

Fig. 7. Calculated transition-state geometry of 8,8'-dimethyl-1,1'-binaphthyl.

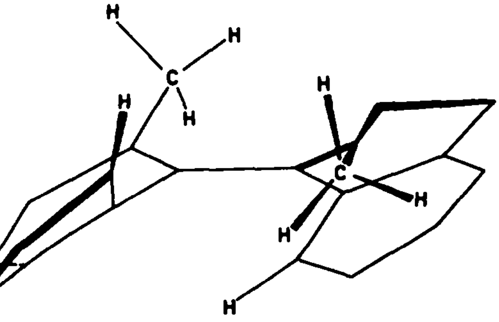

Fig. 8. Calculated transition-state geometry of 2,2'dimethyl-1,1'-binaphthyl.

One important factor intrinsic to the calculational method and relevant to the present discussion is that the energy barriers are calculated from the bottom of a potential well in the initial state to the bottom of a potential well in the transition state. Consequently, the method of calculation makes no allowance for changes in zero-point energy levels between initial and transition states.† For the 8,(8')-series, this could be an acceptable rationalization of the discrepancy in additivity, but since the lack of additivity is so much more pronounced for the 2,(2')-series, according to our calculations, the barrier increments in the latter series could in general be predicted to be non-additive.

CONCLUSIONS

The calculations suggest reasonable sources of energy differences in both initial and transition states for the pairs of molecules studied, and distinctly implicate the operation of the *peri* effect as an important (but not necessarily predominant) contributor to the increased optical lability of the 8- and 8,8'-substituted compounds. Furthermore, initial- and transition-state energy differences are found to be of comparable importance in the determination of the overall energy balance. The calculations clearly show that the degree of torsional and bending distortion required to alleviate the effects of steric crowding are considerably greater in the 2- than in the 8-Me transition state.

The finer points of the calculated results depend of course upon the parametrization of the particular force field employed, but the major qualitative features of, e.g. the differences in transition-state conformation are nevertheless likely to retain their validity.

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[12] cf. discussion by Cooke and Harris (Ref. 6*d*) and by Dixon, Harris and Mazengo (Ref. 6*f*).

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†Our one-dimensional reaction coordinate is admittedly also a great oversimplification, but under the present circumstances it is the only feasible alternative.